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- (54) Process for the production of carboxymethylcellulose with increased solution viscosity
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- (57) This patent is for a process for the production of carboxymethylcellulose in a DS range  $< 1$  with increased solution viscosity. According to the process, the cellulose should be activated with liquid ammonia and then alkalized and carboxymethylized, whereby specific mol ratios and concentrations of the reagents as well as specific mass ratios of the liquid phase, with respect to the cellulose, are established. The conversion occurs in an aqueous organic system. The process can be performed without the need for the relatively expensive or toxic cross-linking agents used in current processes, which has advantages for the solubility of the resulting products. The solution viscosity is increased by a factor of 2 to 5 compared to that of non-activated material. Such products would be technically and economically advantageous as thickeners, adhesives and other agents in the textile, paper, detergent, dye, food, chemical, pharmaceutical and cosmetic industries as well as for many other areas of application.

### Characteristics of invention

#### - Problem definition

The task for the invention is to develop a process to produce CMC in a DS range  $< 1$ , particularly in a range between 0.4 and 0.7 DS, with increased solution viscosity, by alkalization and carboxymethylization of preactivated cellulose in the presence of a partially non-aqueous medium.

#### - Characteristics of the invention

Surprisingly, it was discovered that in the production of CMC with DS values  $< 1$ , particularly in a range between 0.4 and 0.7 DS, an alkalization and carboxymethylization of preactivated cellulose compared to non-activated cellulose yields products whose aqueous solution viscosity values are increased by a factor of 2 to 5.

In this process, cellulose is activated preferably with liquid ammonia and then alkalized with sodium hydroxide, preferably in a range between 0.7 to 4 mol per mol unit of cellulose anhydroglucose, particularly in a range of double the mol number, with respect to use of monochloroacetic acid, plus a small excess of approximately 0.05 mol per mol unit of anhydroglucose.

Furthermore, a liquid which can be mixed with water, for example, a low molecular alcohol such as ethanol or isopropanol, or a ketone such as acetone, is added in an amount that will produce a ratio of cellulose to water preferably in a range of 1:0.5-1.5 parts by weight and a ratio of cellulose to organic liquid in a range of 1:1-10, preferably 1:1-4 parts by weight.

The amount of monochloroacetic acid required in the carboxymethylization process should be between 0.3 and 2 mol per mol unit of cellulose anhydroglucose, which is dissolved after alkalization in a partial amount of the water and/or organic liquid, and then added in the appropriate way, for example by a spray process. The liquid portion is then proportioned out in such a way so that the sodium hydroxide concentration during alkalization is between 6% and the saturation concentration during the liquid phase.

The carboxymethylization process occurs by a rise in temperature and treatment in a temperature range from 20° to 100°C, preferably from 50° to 70°C, until the monochloroacetic acid is almost completely converted in a suitable aggregate unit such as a kneading mixer, for example.

The process according to invention increases the viscosity values by a factor of 2 to 5 for the aqueous solutions produced from the reaction products, in a DS range  $< 1$ , particularly in a range 0.4 to 0.7 DS.

Products in the aforementioned DS range make up a considerably large portion of all manufactured CMC products, especially for those areas of application in which the thickening and/or adhesive effect is/are important. In many cases, a portion of the mostly pelletized gel particles which has not fully dissolved or separated, usually between 5 to 15%, is acceptable.

This process yields products with increased solution viscosity, and for the products with lower DS values in the aforementioned DS range, the amount of undissolved particles is significantly lower. This process does not have the pitfalls and disadvantages associated with current processes, especially with respect to the drop in solubility.

### Application examples

1. 324 parts beech sulfite cellulose are treated for 30 minutes at -50°C with liquid ammonia after which the ammonia residue is steamed off. A mixture of 132 parts sodium hydroxide dissolved in 680 parts 70% ethanol is evenly added to a kneading mixer containing the cellulose activated in this manner. Then it is alkalized at room temperature for 30 minutes. Next 151 parts monochloroacetic acid, dissolved in 427 parts 70% ethanol, are evenly added in for the carboxymethylization process. After 30 minutes of mixing the reaction mixture is heated to 70°C and converted at this temperature for 4 hours. The reaction product is made chloride free by being washed several times with aqueous 80% methanol and then dried.  
A salt free CMC is obtained through centrifugation for 15 minutes under a gravity field of 2000 g which leaves a separable portion of 4.2%, a DS of .057 and a viscosity value (0.1 g CMC in 100 ml cuoxam solution) [illegible] specific /c of 0.226.

In a replication experiment, the non-activated cellulose yields a CMC with practically the same values, and even a separable portion of 4.7%, a DS of 0.60 and [illegible] specific/c of 0.222, however, the viscosity values are noticeably lower. The following dynamic viscosity values for 2% aqueous solutions were ascertained using a rotating viscometer with increasing shear rates (first value in the table) and decreasing shear rates (second value) at 20°C:

Shearing stress, ( $s^{-1}$ )	:	10	20	100	200
(cP), not activated	:	250/210	230/195	170/150	150/135
(cP), activated	:	510/410	430/350	275/250	230/215

- Activated beech sulfite cellulose was alkalized the same way as in example 1, except this time using 100 parts sodium hydroxide, dissolved in 680 parts 70% ethanol, and carboxymethylized as before with 113 parts monochloroacetic acid, dissolved in 427 parts 70% ethanol. The reaction product was washed free of salt and dried. The CMC obtained in this manner had a separable portion of 5.3% with a DS of 0.43. In a replication experiment, the non-activated cellulose yielded a separable portion of 18% with roughly the same DP and a DS of 0.45. The CMC obtained from the activated material showed a considerable increase in viscosity values in the 2% aqueous solution:

Shearing stress, ( $s^{-1}$ )	:	10	20	100	200
(cP), not activated	:	410/310	350/280	240/205	200/180
(cP), activated	:	2320/1700	1700/1320	800/680	570/500

- Sixty-three parts sodium hydroxide, dissolved in 429 parts 70% ethanol are added to a kneading mixer containing 243 parts of activated beech sulfite cellulose over a period of 15 minutes, which is then alkalized for 30 minutes, then 71 parts monochloroacetic acid, dissolved in 401 parts 70% ethanol, are added within 15 minutes and the entire mass is mixed an additional 30 minutes. The reaction mixture is heated to 60°C and converted at this temperature for 3 hours, then it is heated to 80°C and converted an additional hour. From this product the liquid phase is refined at 105°C, thereby completely converting the monochloroacetic acid residue. The CMC which is washed free of salt has a separable portion of 13% with a DS of 0.41. In a replication experiment, the non-activated cellulose yielded a separable portion of 29% with roughly the same DP and a DS of 0.39. The CMC obtained from the activated material showed a considerable increase in viscosity values in the 2% aqueous solution:

Shearing stress, ( $s^{-1}$ )	:	10	20	100	200
(cP), not activated	:	1200/1050	870/770	410/380	300/280
(cP), activated	:	2900/2320	2005/1700	900/800	630/580

### Patent claims

1. Process for the production of carboxymethylcellulose with increased solution viscosity by converting preactivated cellulose, whereby the carboxymethylcellulose is alkalized and carboxymethylized in a DS range  $< 1$ , preferably 0.4 to 0.7 DS, in aqueous organic phase in such a manner so that the mol ratio of a unit of cellulose anhydroglucose to sodium hydroxide is in the preferred range of 1:0.7 to 4, the mol ratio of a unit of cellulose anhydroglucose to monochloroacetic acid is in a range between 1:0.3 to 2, the mass ratio of cellulose to water is 1:0.5 to 1.5 and mass ratio of cellulose to organic liquid is 1:1 to 10, preferably 1:1 to 4, with the water content of the liquid phase being between 15% and 35% and the alkali is added to the cellulose during the alkalization process in a portion of the aqueous organic phase, so that the resulting concentration of sodium hydroxide is between 6% and the saturation concentration.
2. Process according to claim 1, whereby organic liquids which are mixable with water such as low alcohols, preferably ethanol, isopropanol or low ketones, preferably acetone, are used.